MOLECULES IN THE POROUS SYSTEM OF ACTIVATED CARBON FIBERS – SPIN POPULATION CONTROL

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Abstract. The aim of this work is to describe the influence of adsorbed molecules on electronic properties of activated carbon fibers (ACF). Guest molecules of different type, dipolar water molecules and nondipolar CCl_4, were used to analyze the dependence of physisorption forces of pore walls (host-guest interaction) on the localization of spins on ACF graphitic nanoparticles. For each substance the number of localized spins, estimated from electron paramagnetic resonance experiments, was compared to the energy parameter of interaction between guest molecules and pore walls. Control of spin population and potential barriers between nanographitic particles of ACF is important from the point of view of ACF system as a quantum dots matrix.

1. INTRODUCTION

Host-guest interactions in activated carbon fibers (ACF) are of the van der Waals nature [1], and only physisorption is observed in the system. It is also known that molecules adsorbed in porous system of ACF modify the electronic properties of the system of graphitic nanocrystallites building the porous matrix of ACF by increasing the potential barrier for hopping of charge carriers between ACF's nanocrystallites [2,3]. In effect more spins are localized within nanocrystallites allowing detection of electron paramagnetic resonance (EPR) signals of ACF in higher temperature (120-150K) than for pristine ACF (50K). The temperature of metal-insulator transition [4] increases as the host-guest interaction effect.

Different molecules interact with ACF nanographites in a different way. Particularly, the strength of attraction of guest molecules to the pore walls, described by "10-4-3" Steele potential, vary with the change of energy parameters [5,6]. This work is the attempt to show that strength of host-guest interaction depends on the type of molecules adsorbed in pores and influences the electronic properties of ACF. Controlled modification of spin population, by modulation of potential barriers between nanographitic particles, is important if to treat the system of these particles as a quantum dots system [3].

2. EXPERIMENTAL

EPR spectra of ACF were acquired with Radiopan ES/X spectrometer, equipped with Oxford Instruments gas flow helium cryostat, which allows the control of the temperature within 4.2÷300K range. Microwave frequency was measured by microwave frequency counter with an accuracy of 5 kHz. The magnetic field was calibrated by tracking NMR

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magnetometer with an accuracy of 0.005 mT. Fibers were acquired from Osaka Gas Chemicals Co. Ltd, Japan.

ACF sample was evacuated at 200 °C by pumping with turbomolecular pump at 10^{-4} mbar for 1 hour, to assure the pores are empty. Sample was consecutively saturated with guest molecules H_2O or CCl_4. It was necessary to use the same ACF sample for both H_2O and CCl_4 experiments, as ACF is a disordered material and different samples (even of the same weight) have slightly different microstructure, which affects the spin localization. It was shown [7] that desorption process gives the same initial EPR signals for both substances used in the experiment.

3. RESULTS AND DISCUSSION

3.1. Spin number calculation

Spin localization in ACF depends on the adsorbed molecules type and temperature [3]. EPR spectrum of ACF with filled pores consists of three lines [1,2]: line (1), characteristic of pristine ACF and two additional broader components, which are related to different parts of the fiber where:
– rotational motion is supressed because of confinement, giving only slight broadening of the line (2),
– guest molecules rotate freely (surface effect) causing temperature dependent larger broadening of line (3).

This interpretation is in good agreement with results presented in paper [8].

Figs. 2 and 3 show the EPR spectra of ACF with adsorbed H_2O and CCl_4. The number of spins localized in different areas of ACF can be estimated from integral intensities of EPR spectrum components. To get the information about the spin number, α,α-diphenyl-β-picrylhydrazyl (DPPH) standard, with $115·10^6$ spins, was used, see Fig. 1. DPPH powder spectrum consists of single, narrow Lorentzian line, detected at $g = 2.0036$ [9].

For both substances adsorbed in ACF we get similar number of spins for line (1). This result confirms that line (1) origins from nanocrystallites that have no contact with guest molecules (pure ACF areas). In case of line (2), for both experiments, significant differences have been observed. The number of spins localized in nanocrystallites building walls of ACF pores filled with CCl_4 is much lower than in case of H_2O adsorption (Table 1). We do not estimate the number of spins for line (3), because this line is much broader than observed for DPPH standard, and the line is dynamically broadened because of surface effect [10]. Estimation was made for ACF with adsorbed CCl_4 and H_2O. Because of Curie law, spectra was taken in the same temperature of 20K.
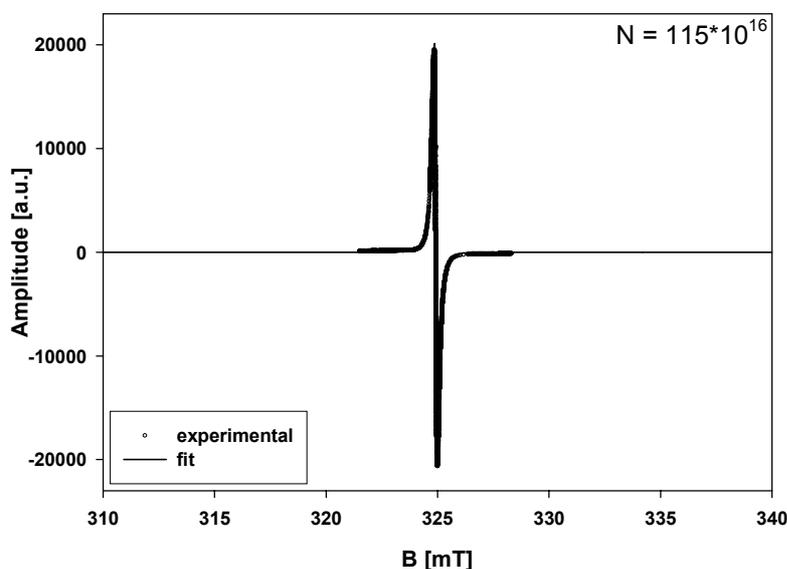

Fig. 1. EPR spectrum of powdered DPPH – single Lorentzian line with $115·10^{16}$ spins.
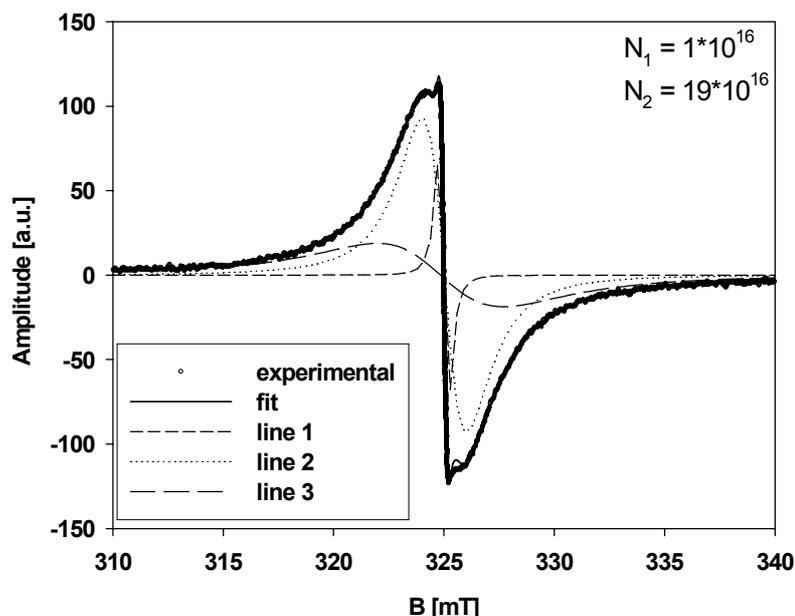
Fig. 2. EPR spectrum of ACF with adsorbed H_2O at 20K with three fitting lines.

3.2. Host-guest interaction strength

In previous papers [5,6] ACF's physisorption strengths for H_2O and CCl_4 were calculated using "10-4-3" Steele potential of the form:

$$\phi_{fw}(z) = 2\pi\rho_w\varepsilon_{fw}\sigma_{fw}^2\Delta\left[\frac{2}{5}\left(\frac{\sigma_{fw}}{z}\right)^{10} - \left(\frac{\sigma_{fw}}{z}\right)^4 - \left(\frac{\sigma_{fw}^4}{3\Delta(z+0.61\Delta)^3}\right)\right], \quad (1)$$

where: ε_{fw}– energy parameter determining the depth of the potential well for fluid-wall (guest-host) interaction, σ – size parameter – distance between two particles where the potential reaches zero, ρ – number density of the pore walls atoms, Δ – distance between two successive lattice planes, z – coordinate perpendicular to the pore walls.

Values of energy parameter for fluid-wall (host-guest) attraction ε_{fw} for H_2O and CCl_4 were calculated from Lorentz-Berthelot mixing rule, using data from [5,6]:

$$\varepsilon_{fw} = \left(\varepsilon_{ff} \cdot \varepsilon_{ww}\right)^{1/2}, \quad (2)$$

where: ε_{ff}, ε_{ww} are the Lennard-Jones parameters for fluid (guest) and pore walls (host) respectively. The values are shown in Table 2, together with the number of localized spins calculated from integral intensity of the line (2) of EPR spectra of ACF filled with both substances. ε_{fw} for ACF+H_2O is larger than for ACF+CCl_4 as it is in case of the localized spin number. For stronger interacting H_2O mol-

Table 1.

ACF + H_2O	ACF + CCl_4
$N_1 = 1\cdot10^{16}$	$N_1 = 1\cdot10^{16}$
$N_2 = 19\cdot10^{16}$	$N_2 = 3\cdot10^{16}$

Table 2.

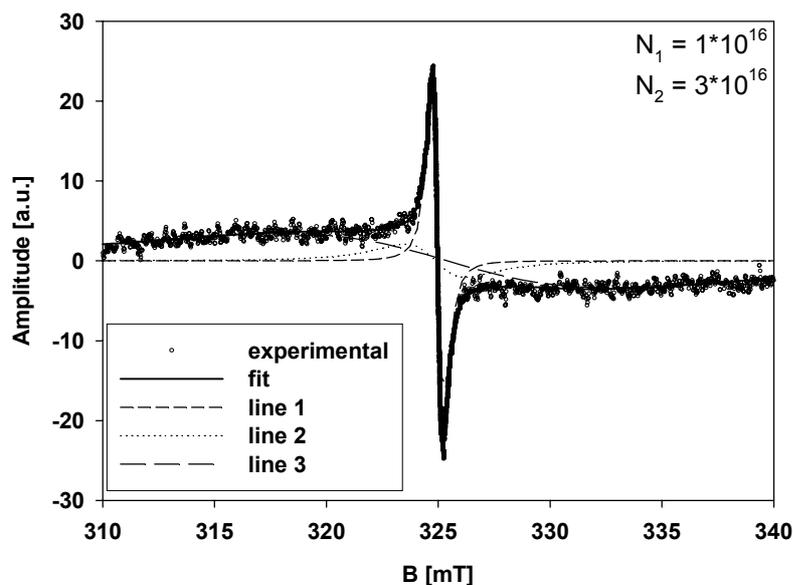| ACF + H_2O	ACF + CCl_4
$\varepsilon_{ww} = 28\ k_B/K$	$\varepsilon_{ww} = 28\ k_B/K$
$\varepsilon_{ff} = 888\ k_B/K$	$\varepsilon_{ff} = 366\ k_B/K$
$\varepsilon_{fw} = 157\ k_B/K$	$\varepsilon_{fw} = 101\ k_B/K$
$N_2 = 19\cdot10^{16}$	$N_2 = 3\cdot10^{16}$

Fig. 3. EPR spectrum of ACF with adsorbed CCl_4 at 20K with three fitting lines.

ecules we get more localized spins in graphitic nanoparticles building pore walls, which have the closest contact with guest molecules.

4. CONCLUSIONS

The attempt to compare the host-guest interaction strength with the influence of guest molecules on charge transport properties in ACF was made. Results indicate that stronger interacting dipolar H_2O molecules cause more carriers to be trapped in localized states than it is observed for nondipolar CCl_4. The adsorbed substances have significant influence on electronic properties of ACF porous graphitic system. This effect could be used for stimulation or even control the potential barriers in the porous system of ACF treated as a quantum dots matrix.

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